ANALYSIS OF PARTIALLY CONVERTED LIGNOCELLULOSIC MATERIALS

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ABSTRACT

The systematic analysis of the solid residues of the supercritical methanol extraction of Populus tremuloides was performed for samples prepared at temperatures varying from 250 to 350°C and pressures from 3.4 to 17.2 MPa, using such analytical techniques as wet chemistry, chromatography, thermogravimetric analysis, diffuse reflectance FTIR spectroscopy and photoelectron spectroscopy. The results allow to monitor the continuous changes in chemical composition of the samples from partly extracted wood samples to highly recondensed polyaromatic structures.

INTRODUCTION

In the recent studies of thermal and thermochemical processes of wood liquefaction, considerable progress has been reported in the analysis of gazeous and liquid products [1]. Some attention has been given to the composition of the solid products by wet chemistry analysis [2,3].

For the last twenty years much work has been done in the study of the thermal stability of lignocellulosic materials by thermal analytical methods. Since these materials are complex mixtures of organic polymers, thermogravimetric (TG) analysis causes a variety of chemical and physical changes depending on the nature of the sample and its treatment prior to analysis. These problems have been reviewed recently [4].

Lignocellulosic material can also be analyzed by IR spectrometry. This analytical method was used, for characterization of modified lignin and cellulose in various ways [5-13]. Quantification by infrared spectrometry, has been reported, for example in analysis of the three basic constituents in sweetgum and white oak chips pretreated at temperatures ranging from 140 to 280°C[5] using the diffuse reflectance FTIR spectrometry (DRIFT). The technique is simple and applicable to powdered solids and dark samples[14] and can be used for the characterization of the chemical bonds and their modifications by thermal processes.

In this paper we report our efforts to characterize the solid residues produced in a series of experiments for the semicontinuous extraction of Populus tremuloides in supercritical methanol[15], at temperatures ranging from 250 to 350°C (Supercritical Extraction residues or SCE residues), by using wet chemistry and chromatographic[16], thermogravimetric and spectral methods such as DRIFT[17] and ESCA[18].

EXPERIMENTAL PROCEDURE

The solid residues analyzed here were produced by supercritical extraction with methanol of Populus tremuloides in a tubular reactor[15]. The analytical procedures used for these residues were described previously as elemental analysis, Klason lignin test, thioglycolic acid lignin test, recondensed material and carbohydrates[16], thermogravimetric (TG/DTG) and FTIR[17] and ESCA[18]. Table 1 reports results obtained using these procedures as well as conditions of extraction for each SCE residues.

RESULTS AND DISCUSSION

Wet Chemistry and Chromatography

For the analysis of wood, the Klason lignin test, performed in concentrated sulfuric acid, is the accepted method for the determination of lignin content. We performed similar tests using also trifluoroacetic acid (TFA), the results of which are almost identical to those of the Klason tests. TFA has the advantage to allow further analysis of the saccharides in the acid soluble fraction as it can easily be evaporated from the solution.

The acid insoluble fraction, usually designated as "Klason lignin", is referred to in this work as Klason residue. Figure 1 shows that in the most severe extraction conditions the whole SCE residue is almost entirely constituted of Klason residue. The fact that this Klason residue cannot be considered as lignin has been established through elemental analysis and IR spectroscopy in KBr pellets[16].

In order to determine if the solid residues still contain lignin the old method of forming a soluble lignin derivative with thioglycolic acid was used. This reagent reacts by displacement of α-hydroxyl and α-alkoxyl groups in lignin and the derivative so produced can be solubilized by alkali and recovered. Results are reported in Table 1 and Figure 1 showing that thioglycolic acid lignin (TGAL) decreases from 15.6% in wood to 3.3-5.9% in the samples prepared at 350°C. It was shown by IR spectrometry that the TGAL keeps the characteristic features of lignin even for SCE temperatures of 350°C[16].

This confirms our belief that the thioglycolic acid test is a suitable method for the determination of uncondensed lignin in SCE residues. In spite of the fact that 1) the Klason test induces some condensation reactions, 2) the thioglycolic acid test may only extract those lignin fragments containing benzyl alcohol groups or aryl ether groups[19], we would like to suggest that
1) the thioglycolic acid lignin represents a good estimate of unconverted lignin,
2)the Klason residue represents the summation of unconverted lignin and of condensation products formed by pyrolysis reactions during the SCE process.

As a consequence we suggest that the difference between the Klason residue and the thioglycolic acid lignin is representative of recondensed material (RM) in SCE residues. The calculated values for recondensed material in these residues are reported in Table 1. Figure 2 gives the values for the percent recondensed material expressed on a dry wood basis.

Figure 3 shows the pereentage of recondensed material, expressed on dry wood basis, plotted as a function of lignin conversion. This graph suggests different condensation reactions at 250°C and at 300-350°C. At 250°C in particular, the condensation seems to be a secondary reaction of lignin conversion. As also shown on the figure, for several experiments the percents of recondensed material are higher than the value which would be calculated assuming that all converted lignin is transformed to recondensed material (line A). It is believed that this indicates that the condensation reaction involves not only products of degradation of lignin but also some of carbohydrates.

The glucose and xylose contents were determined in the soluble TFA acid hydrolysis fraction by liquid chromatography using a cation exchange resin (Ca^{++} form) column. The results are reported in Table 1. Most of the samples prepared at 300-350°C show only minor amounts of hydrolyzed material except for samples MP-16, MP-13 and MP-14 prepared at low pressure or low flow rate. The percents of glucose and xylose for these samples as well as those for the samples prepared at 250°C, expressed on dry wood basis, are plotted on Figure 4. The rather well defined curve indicates that cellulose and hemicellulose are simultaneously degraded at or below 250°C.

Thermogravimetric Analysis

Thermogravimetric analysis (TG and DTG) under nitrogen atmosphere was performed for aspen wood and the 16 partially converted wood residues. The TG and DTG curves are reproduced in Figure 5 for untreated wood and for 4 selected representative SCE residues.

The examination of TG and DTG curves, shows that:
a) aspen wood loses weight starting near 230°C (pyrolysis of hemicellulose [21]), and between 350 and 420°C with a maximum rate of weight loss at 385°C (cellulose and lignin pyrolysis [21]); the weight lost at 700°C is 89.4%.
b) the SCE residues can be classified according to their temperature of extraction.

For the residues of type I prepared at 250°C (like sample MP-6), the weight loss takes place between 350 and 420°C, with a maximum rate at 375-390°C. The weight lost at 700°C is between 82.5 and 94.6%.

For the type II residues produced at 300°C (like sample MP-12), a continuous weight loss is observed from 300 to 600-700°C, with a maximum rate at temperatures ranging from 380°C to 510°C. The total weight loss at 700°C is less important than for samples of the previous type, ranging from 27.2 to 57%.

For samples of type III prepared at 350°C (like samples MP-11 and MP-8), the weight loss is slower than for those of type II but happens roughly on the same temperature range (300 to 600-700°C) and with maximum rates occuring at higher temperatures, from 380 to 620°C. The weight loss at 700°C is significantly smaller ranging from 8.2 to 34.2%.

A closer analysis of these curves shows that there is a continuous change in the shape of the thermogram of the residues as the SCE pressure is increased for experiments at the same SCE temperature. As shown in Figure 6 the temperature T_{max} corresponding to a maximum on the DTG curve shows a continuous evolution with the parameters of extraction. Two maxima are observed at the lower SCE pressure of 3.4 MPa showing that when the extraction is performed less efficiently, some of the unconverted lignin and cellulose is still present at relatively high content in the residue prepared at 350°C.

The smooth evolution in the temperature of the high temperature DTG peak reflects a change in the nature of the volatile fraction of the recondensed material.

A very good correlation was found between weight lost between 200 and 420°C and the weight of trifluoroacetic acid soluble plus unconverted lignin previously determined by wet chemistry (correlation coefficient is 0.994 if one excepts sample MP-16). These data suggest that the material still not volatilized at 420°C would be identical with what we defined as the recondensed material. It was indeed verified that the correlation between recondensed material and weight % of the solid not volatilized at 420°C is also excellent (correlation coefficient 0.984 when point MP-16 is excepted). From thermogravimetric data the recondensed material in a given SCE residue can thus be further characterized by the weight fraction of RM volatilized between 420 and 700°C.

Diffuse Reflectance Infrared Spectrometry

DRIFT spectra were obtained for the 17 afore mentionned samples and the spectra of the five representative samples used to present the TG/DTG data, are reported in Figure 7.

The spectrum of aspen wood (Figure 7.A) shows the presence of the three fundamental wood constituents. The bands for cellulose are at 898 cm^{-1} (β-anomer in pyranose ring) [22], at 1043-1171 cm^{-1} (C-O bonds in primary and secondary alcohols). The

band at 1745 cm^{-1} is due to uronic acid and acetyl groups in hemicellulose [22]. The bands from 1246 to 1607 cm^{-1}, specially the one at 1505-1515 cm^{-1}, are typical for lignin [19].

As shown by the other spectra in Figure 7, these bands are significantly modified by the SCE treatment.

Spectral region 2850-3050 cm^{-1}. A band at 3050 cm^{-1} (aromatic and/or alkene C-H stretching) becomes evident at 300°C (MP-12, Figure 7-C) and dominates this region at 350°C (MP-8, Figure 7-E). The band in the 2900 cm^{-1} region (aliphatic C-H stretching) which is broad in the initial wood sample, is progressively resolved in three separate bands (2850, 2900 and 2950 cm^{-1}) as the SCE temperature is increased (MP-12, MP-11 and MP-8, Figures 7C, D and E). The overall pattern in Figure 7E corresponding to the most carbonized sample is similar to the ones reported for higher rank bituminuous coal [23] and for vitrinite [24], with the 3050 cm^{-1} even more intense in our MP-8 sample. As it was shown earlier that this sample contains 89.2% of recondensed material it may be concluded that this material has a coal-like polyaromatic nature. This is supported by the changes in the next spectral region.

Spectral Region 800-950 cm^{-1}. The band at 898 cm^{-1} is discernible in wood and MP-6 (SCE temperature 250°C) but disappears from spectra of samples treated at higher temperatures where saccharides analysis has also shown the absence of cellulose. As carbonization proceeds, the out-of-plane bending of one isolated (868-874 cm^{-1}) and two adjacent (815-816 cm^{-1}) aromatic H increase.

The band at 950 cm^{-1}, which is visible in MP-8, is probably due to elimination reaction giving t-alkenes[19].

Spectral Region 1440-1600 cm^{-1}. The characteristic aromatic ring vibration at 1505-1515 cm^{-1}, clearly visible in the spectrum of wood, is gradually hidden with an increase in the SCE temperature. This corresponds to the progressive decrease in lignin content of the residue. Inversely, two bands at 1443-1461 and 1600 cm^{-1} become very intense and dominate in the spectra of residues produced at 300 and 350°C (Figures 7-C, D and E). These changes parallel the modifications in the 2850-3050 cm^{-1} region. The band at 1443-1461 cm^{-1} can be attributed to methyl and methylene bonding and also to aromatic ring modes [24,19]. The band at 1600 cm^{-1} is also assigned to aromatic ring stretching. Its high intensity in spectra 7-C, D and E, could possibly be given the three following explanations [24]:
1) aromatic ring stretching in combination with a chelated conjugated carbonyl structure, 2) aromatic ring stretching mode, with possible intensity enhancement due to phenolic groups, 3) aromatic ring stretching of aromatic entities linked by methylene and possibly ether linkages.

Spectral Regions 1035-1378 and 1700-1745 cm^{-1}. The bands from 1035 to 1171 cm^{-1} (primary and secondary alcohols), present in wood and samples obtained at 250°C, drop in the spectra of SCE residues produced at and above 300°C. The aromatic ethers bands (up to 1378 cm^{-1}) which include phenolic stretching near 1250 cm^{-1}, decrease also.

The hemicellulose band, at 1745 cm^{-1}, present on untreated wood almost disappears in residues prepared at 250°C. The unconjugated carbonyl and/or carboxyl and/or ester of conjugated acids at 1720-1735 cm^{-1} from original lignin is still visible at 250°C when hemicellulose is partly removed but at higher SCE temperatures it is hidden by the highly intense 1700 cm^{-1} band. This last band can be attributed to a conjugated carbonyl or carboxyl structure but it would be surprising that carboxyl could resist at severe SCE conditions. Further study is necessary for definite assignment of this band.

Quantification. Schultz et al[5] reported recently correlations of FTIR absorbance ratios with such variables as the percents in glucose, xylose and Klason lignin for

wood chips pretreated by the RASH process at temperature ranging from 140 to 280°C. These correlations do not fit correctly our data so that we developped our own equations by non-linear least squares regression. For quantitative evaluation of absorbances, baseline was defined as shown on spectrum 7E.

These equations are as follows.

$$\% \text{ Klason Lignin} = 174.6 - \left(101 \times \frac{A2950}{A1376}\right) + \left(150.4 \times \frac{A2850}{A1376}\right) - \left(196.7 \times \frac{A1720}{A1376}\right) + \left(223.4 \times \frac{A1700}{A1376}\right) - \left(198.1 \times \frac{A1245}{A1376}\right) \quad (1)$$

$$\% \text{ Unconverted Lignin} = -17.13 + \left(17.53 \times \frac{A2900}{A1429}\right) + \left(20.77 \times \frac{A1505}{A1429}\right) - \left(99.18 \times \frac{A1090}{A1429}\right) + \left(122.2 \times \frac{A1043}{A1429}\right) + \left(48.72 \times \frac{A895}{A1429}\right) \quad (2)$$

$$\% \text{ Recondensed mat.} = 242.2 + \left(263.8 \times \frac{A1330}{A1090}\right) - \left(240.7 \times \frac{A1245}{A1090}\right) - \left(273.4 \times \frac{A1043}{A1090}\right) - \left(327.6 \times \frac{A895}{A1090}\right) - \left(45.62 \times \frac{A868}{A1090}\right) \quad (3)$$

$$\% \text{ Glucose} = -33.07 + \left(74.06 \times \frac{A1505}{A1461}\right) - \left(46.28 \times \frac{A1376}{A1461}\right) - \left(84.12 \times \frac{A1330}{A1461}\right) + \left(74.39 \times \frac{A1245}{A1461}\right) + \left(65.39 \times \frac{A1130}{A1461}\right) \quad (4)$$

$$\% \text{ Xylose} = -51.54 - \left(17.74 \times \frac{A1700}{A1429}\right) + \left(38.53 \times \frac{A1600}{A1429}\right) + \left(18.17 \times \frac{A1245}{A1429}\right) - \left(13.44 \times \frac{A1171}{A1429}\right) + \left(40.60 \times \frac{A1130}{A1429}\right) \quad (5)$$

Calculated results for the 16 samples of SCE residues showed standard deviations from experimental values of 5.12, 1.28, 4.96, 3.62 and 1.62% and correlation coefficients of 0.99, 0.97, 0.99, 0.98 and 0.98 for equations (1) to (5) respectively.

ESCA

ESCA is a surface sensitive technique, based on the measurement of kinetic energies of photoelectrons ejected from a given atomic energy level under the action of a monoenergetic X-ray beam. It provides quantitative information on the elemental composition as well as on the chemical environment of each atom (bonding and oxidation state).

The kinetic energy of photoelectrons (E_K), as measured with respect to the vacuum level, is expressed as:

$$E_K = E_X - (E_B + \phi + E_C) \quad (6)$$

where E_X is the energy of the incident photon, E_B is the binding energy of the electron on its original level, ϕ is the work function of the spectrometer and E_C is the energy lost in counteracting the potential associated with the steady charging of the surface. ϕ and E_C are essentially corrections. ϕ is depending on the spectrometer and not liable to be modified between experiments. E_C is high on low conductivitiy samples and can be made lower by the use of a flood gun.

ESCA spectra corresponding to carbon 1s peaks of Populus tremuloides, 3 samples isolated at three different SCE temperatures and 2 reference compounds are illustrated in Figure 8. There is a general agreement in the literature on the assigment of components C_1, C_2 and C_3 in wood derived materials: C_1 corresponds to carbon linked to H or C, C_2 has one link to oxygen, whereas C_3 has two. In the solid phase, C_1 is referenced at 285.0 eV and C_2 and C_3 are usually close to 287.0 and 289.5 eV (25).

In all SCE residues, a fourth C_{1s} component is found on the low binding energy side of the spectrum, shifted from the C_1 component by 1.4 ± 0.5 eV. This is thereafter

designated as the C_o component. As the temperature of extraction is increased from 250 to 300°C, the C_o component increases continuously whereas the general trend of C_1, C_2 and C_3 components in a continuous decrease.

It is interesting to note that the uncorrected experimental C_{1s} binding energy for dibenz (a,h) anthracene is very close to the binding energy for this C_o peak. As polyaromatic are electrical conductors, the charging is expected to be low and E_c close to 0. On this basis, C_o component is assigned to carbon in polyaromatics. Usually, aromatic compounds show a shake up satellite located 5-7 eV above their C_{1s} peak [28]. It can be seen however from Figure 8 that the intensity of this satellite in dibenz (a,h) anthracene is considerably lower than in o-biphenol. Thus the satellite from C_o peak in SCE solid residues should only make a minor contribution to the overall C_{1s} band.

The ratio C_{RM}/C_{SR} (where C_{SR} is the carbon content of the whole solid residue as determined by elemental analysis, whereas C_{RM} is the calculated mass of carbon in the recondensed material contained in a given sample) was calculated for 5 samples (the elemental analysis for MP-13 was not available). Figure 9 shows not only that this ratio is correlated to the C_o fraction of the C_{1s} peak, but that both values are almost equal for all samples.

Therefore it may be concluded that the ESCA technique provides a simple mean for the determination of the extent of recondensation reactions by a mere determination of the proportion of the C_o component in the C_{1s} band of the solid residue.

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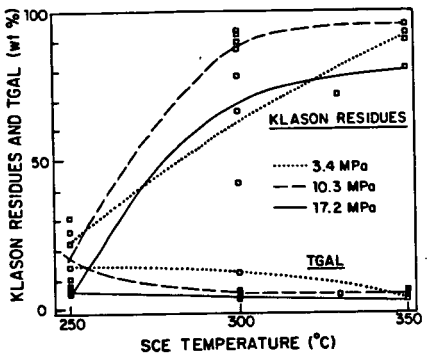

Figure 1. Klason residues and Thioglycolic acid lignin in SCE solid residues.

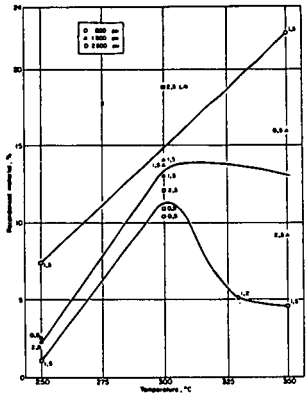

Figure 2. Effect of SCE conditions on recondensed material (expressed on dry wood basis).

Sample	SCE Temperature °C	SCE Pressure MPa	SCE Flowrate l/h	Residue yield wt%	Klason residue wt%	TGAL wt%	Recond. material wt%	Klason soluble wt%	Glu wt%	Xyl wt%	% C	% H	% O
Wood	-	-	-	100.0	17.6	15.6	-	78.5	47.6	27.2	46.1	6.50	47.4
MP-22	250	3.4	1.5	74.8	26.1	14.3	11.8	70.8	45.7	18.0	50.0	5.84	44.2
MP-6	250	10.3	0.5	55.4	38.5	22.2	8.3	64.1	38.1	12.8	53.5	5.29	41.2
MP-17	250	10.3	2.5	69.7	10.6	6.5	4.1	89.9	38.0	19.2	45.0	6.49	48.6
MP-15	250	17.2	1.5	68.4	7.6	5.4	2.0	90.6	26.9	12.3	44.1	6.97	48.9
MP-16	300	3.4	0.5	40.5	42.2	12.1	30.1	46.4	25.9	7.9	64.9	5.82	29.2
MP-20	300	3.4	2.5	31.0	78.1	12.3	65.8	-	0.0	0.0	75.9	5.12	19.0
MP-9	300	10.3	1.5	16.4	92.1	4.3	87.8	5.0	0.0	0.0	78.2	4.96	16.8
MP-12	300	10.3	1.5	15.9	92.5	3.8	88.7	1.6	0.6	0.0	80.4	4.62	15.0
MP-21	300	10.3	1.5	15.7	89.2	4.5	84.7	2.4	0.0	0.0	79.8	5.35	14.8
MP-13	300	17.2	0.5	18.4	65.8	6.0	59.8	27.2	10.3	3.3	64.8	5.47	29.7
MP-18	300	17.2	2.5	15.0	86.7	5.3	81.3	4.0	0.7	0.0	73.3	5.17	21.6
MP-27	330	17.2	1.2	8.4	71.4	4.8	66.7	19.8	7.1	0.0	74.1	6.08	19.8
MP-14	350	3.4	1.5	26.9	90.0	5.2	85.1	11.1	4.8	1.5	74.8	4.34	20.8
MP-11	350	10.3	0.5	18.2	92.3	3.8	88.5	0.8	0.0	0.0	83.5	4.89	11.6
MP-8	350	10.3	2.5	10.2	95.1	5.9	89.2	1.2	0.0	0.0	92.8	3.84	3.33
MP-24	350	17.2	1.5	6.1	80.3	3.3	77.0	3.1	0.0	0.0	76.3	5.00	18.8

Table I. SCE residues, extraction conditions and analyses

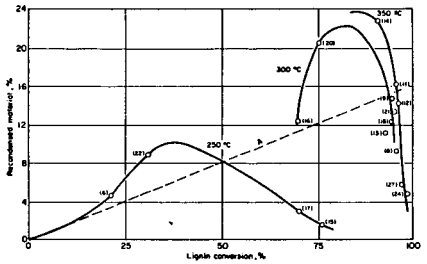

Figure 3. Recondensed material (expressed on dry wood basis) as a function of lignin conversion

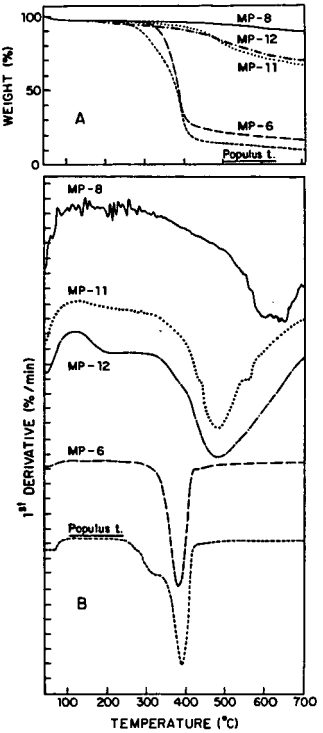

Figure 5. Thermogravimetric analysis of Populus trg muloides and of four SCE residues; TG (A) and DTG (B) in flowing nitrogen.

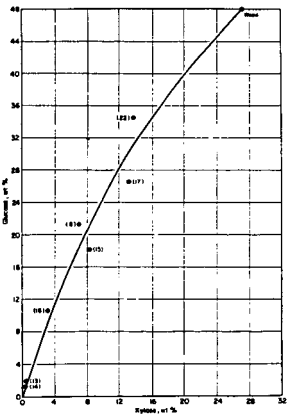

Figure 4. Residual hydrolyzed glucose as a function of residual hydrolyzed xylose (both expressed on dry wood basis).

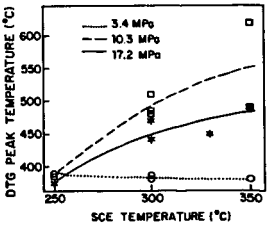

Figure 6. DTG peak temperature as a function of SCE temperature and pressure.

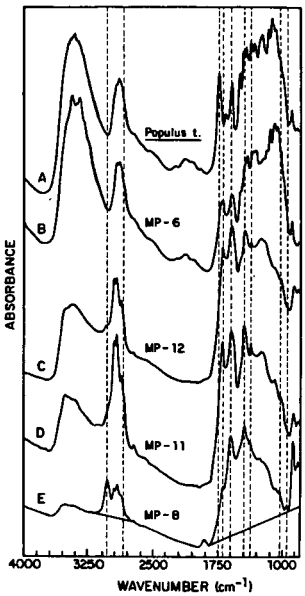

Figure 7. DRIFT spectra of the same samples as in Figure 5.

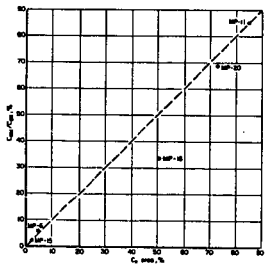

Figure 9. Relation between carbon in recondensed material and polyaromatic carbon from ESCA C_{1s} peaks

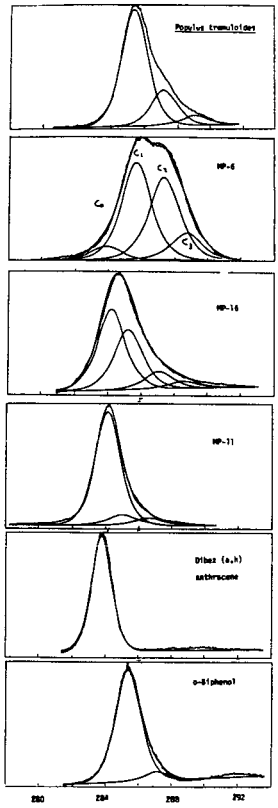

Figure 8. ESCA spectra (C_{1s} peaks) of Populus tremuloides, of 3 (three) SCE residues and of two standards compounds